DESCRIPTION

Carrier Having Alumina Coated Thereon, Catalyst Element, and
Method for Preparation of Carrier Having Alumina Coated
Thereon

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Technical Field

        The present invention relates to a carrier having
alumina coated thereon, a method for production of the
catalyst, and a catalyst body. More particularly, the
10   present invention relates to a carrier which is used for
coating a catalytic material typical for a NO_x adsorption
catalyst for purification of automobile exhaust gas,
containing an alkali metal or an alkaline earth metal,
particularly Li, Na, K or Ca, and which can be used for
15   production of a catalyst body wherein the deterioration of
the carrier caused by an alkali metal or alkaline earth metal
is suppressed and, even in use over a long period of time
with a catalytic material coated on the carrier, there occurs
substantially no deterioration of the carrier by the
20   catalytic material; a method for production of the carrier;
and a catalyst body comprising the carrier and, for example,
a catalytic material (typical for a NO_x adsorption catalyst)
coated thereon, containing an alkali metal or an alkaline
earth metal, particularly Li, Na, K or Ca.

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Background Art

        In recent years, regulation for exhaust gas has been
intensified and lean burn engine, direct injection engine,
etc. have come into wide use. In this connection, NO_x
30   adsorption catalysts capable of purifying the NO_x present in

exhaust gas effectively in a lean atmosphere have been put into practical application. As the NO_x adsorption component used in such a NO_x adsorption catalyst, there are known alkali metals such as K, Na, Li, Cs and the like; alkaline

5   earth metals such as Ba, Ca and the like; rare earth elements such as La, Y and the like; and so forth. Ba, in particular, is in wide use since the beginning of practical application of NO_x adsorption catalysts. Recently, K which is superior in NO_x adsorption capability in a high-temperature range has

10   been tried for use.

NO_x adsorption catalysts are generally constituted by coating a catalytic material containing the above-mentioned NO_x adsorption component, on a carrier made of an oxide type ceramic material (e.g. cordierite) or a metal material (e.g.

15   Fe-Cr-Al alloy). Such a carrier, however, has a problem in that it is liable to be corroded and deteriorated by alkali metals or some alkaline earth metals, particularly Li, Na, K and Ca when these metals have become active under a high-temperature exhaust gas. In particular, a cordierite carrier

20   made of an oxide type ceramic material reacts with the above mentioned alkali metal or the like and generates cracks, which is a serious problem.

In catalyst bodies for purification of exhaust gas, active alumina has heretofore been used as a carrier matrix

25   having a high specific surface area, for highly dispersing a catalytically active component represented by a noble metal or the like. However, the present invention differs in that, in a catalyst body comprising a carrier and a catalytic material coated thereon, containing an alkali metal and/or an

30   alkaline earth metal, alumina is precoated on the carrier

before catalyst loading in order to protect a carrier represented by cordierite honeycomb, from its contact and subsequent reaction with an alkali metal and/or an alkaline earth metal both present in a catalyst layer.

5   The present invention has been made in view of such conventional problems and aims at providing a carrier suitable for coating a catalytic material containing an alkali metal or alkali earth metal, for example, a NO_x adsorption catalyst and, when used as a catalyst body,

10   capable of suppressing the carrier deterioration caused by the alkali metal or alkaline earth metal and usable over a long period of time; a method for production of the carrier; and a catalyst body comprising the carrier and a catalytic material coated thereon.

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Disclosure of the Invention

         According to the present invention, there are provided a carrier suitable for coating thereon a catalytic material containing an alkali metal and/or an alkaline earth metal,

20   wherein alumina is disposed in the carrier or on the cell wall surface of the carrier; and a catalyst body comprising the carrier and a catalytic material coated thereon.

         According to the present invention, there is also provided a method for producing a catalyst having alumina

25   coated thereon, characterized in that it comprises a step of coating alumina on a carrier and, optionally, a step of coating on the carrier a substance liable to react with an alkali metal and/or an alkaline earth metal both used as a catalytic material and/or an alkali metal and/or an alkaline

30   earth metal and further in that the thus-obtained carrier

having alumina and, optionally, such a substance and such a metal, coated thereon, is fired.

Best Mode for Carrying Out the Invention

5   In the present invention, alumina low in reactivity with an alkali metal and/or an alkaline earth metal both used as a catalytic material is disposed beforehand in a carrier and/or on the cell wall surface of the carrier. Thereby, the carrier is protected by alumina from the alkali metal and/or

10   the alkaline earth metal even when a catalyst body comprising the carrier and a catalytic material coated thereon is exposed to high temperatures during the use, and the reaction of the carrier with such metals is suppressed; as a result, the deterioration of the carrier is suppressed.

15   Alumina is known to have various phases. In the present invention, the stability of alumina is important and γ-alumina, δ-alumina, η-alumina, θ-alumina, α-alumina, amorphous alumina or the like are suitable for use. In general, α-alumina is preferred for the high corrosion

20   resistance depending upon the environment of carrier used; amorphous alumina is preferred because it easily forms a dense protective film; and γ-alumina is preferred because it has good affinity with the catalytic material used. A desired effect is obtainable substantially irrespective of

25   the kind of the alumina phase used, as long as an alumina layer of intended thickness is formed, which is a surprise.

Incidentally, individual phases of alumina may be disposed singly or in combination of a plurality of phases. For example, mixed disposition of α phase and amorphous

30   phase or of γ phase and amorphous phase is preferred because

the property of α phase or γ phase is exhibited, in addition to the high density derived from amorphous phase.

As to the form of alumina when disposed, there is no particular restriction, and alumina may be disposed by itself

5 or in a composite or mixture with other substance. However, from the standpoint of corrosion resistance, it is preferred to dispose alumina in a concentration of 90% by mass or more and is more preferred to dispose substantially alumina alone, in other words, only alumina. When other component is used

10 in a composite or a mixture, it is preferred to select a component which per se has a high corrosion resistance to alkali metals and/or alkaline earth metals, or a component capable of increasing the corrosion resistance and heat resistance of alumina.

15 Incidentally, as the source of alumina, an alumina powder, preferably an alumina sol, more preferably an alumina powder and an alumina sol, further preferably substantially an alumina powder and an alumina sol alone are used. The alumina source is preferred to be substantially an alumina

20 sol alone because its coating on the carrier can form a dense alumina layer. Also, coating of an alumina sol and an alumina powder is preferred because, as compared with the coating of an alumina sol alone, a higher firing temperature can be employed, no crack is generated on the surface of the

25 formed alumina coat, and a required amount of alumina can be coated with less coating times. The kind of alumina used, coating method, firing conditions, etc. are described in detail below.

The specific alumina source used is selected

30 appropriately depending upon the coating method used. For

example, when coating is conducted using a solid (a powder),
an oxide or the like is used; when coating is conducted using
a liquid (a solution or a dispersion), a solution or
dispersion of a nitrate, a sulfate, a hydroxide, a chloride,

5   an organic acid salt, an alumina sol or the like is used (the
liquid is hereinafter referred to as "alumina source-
containing liquid"). Of these, there is preferred an alumina
source which leaves no component other than alumina in the
catalyst body obtained, in treatments such as firing and the

10   like. As the method for disposing alumina in the carrier
and/or between the carrier and the catalytic material coated
thereon, the following methods can be mentioned.
[Method for disposing alumina in carrier]

       By immersing a carrier in an alumina source-containing

15   liquid of relatively low viscosity, it is possible to
infiltrate the liquid into a so-called virgin carrier (not
coated with any catalyst or the like) to dispose the alumina
source in the carrier. This method is used preferably when
the carrier is porous, and can introduce an alumina source

20   even into each open pore. There may also be used a method of
adding an alumina source to the raw materials of carrier at
the stage of carrier production. In this case, the alumina
source may be added in the form of a solution or a dispersion
or in the form of a solid (a powder) such as oxide or the

25   like. The added alumina source may form a compound with
other raw materials in the carrier production stage, but it
is preferable that alumina remains as it is. Of the method
of immersing a carrier in an alumina source-containing liquid
and the method of adding an alumina source to carrier raw

30   materials, the former immersion method is preferred because

the exposure of carrier, i.e. the contact of carrier with
alkali metal and/or alkaline earth metal in catalytic
material is prevented. As a matter of course, the carrier
can have the highest corrosion resistance when it is made of
5   alumina per se; however, in this case, in order for the low
thermal shock resistance of alumina to cause no problem, it
is necessary, for example, to make temperature control during
the use of carrier or restrict the application of carrier.
[Method for forming alumina-containing precoating layer on
10 cell wall surface of carrier]

Unlike the case of disposing alumina in a carrier,
there is substantially no influence of the structure of the
carrier used. In a specific method, a carrier is coated with
a solution or dispersion of relatively high viscosity,
15 containing an alumina sol or the like, whereby alumina can be
disposed as a precoating layer between the carrier and a
catalytic material layer for exhibiting a desired effect.
Use of an alumina sol (50wt% by the solid content or more,
preferably 90wt% or more of the total) as an alumina source
20 is preferred because it can easily form a dense precoating
layer. Use of substantially an alumina sol alone is more
preferred.

As other method, an alumina powder, for example, is
made into a slurry and the slurry is coated to form a
25 precoating layer. There is also preferred a method of adding,
in the slurry making, an organic binder and/or an inorganic
binder, because the precoating layer formed is less
susceptible to peeling. An alumina sol, in particular, is
most preferred because it increases the proportion of alumina
30 in precoating layer and also contributes to an increase in

density. As the alumina powder, various phases such as mentioned above may be used suitably. Further, a plurality of kinds different in phase, particle diameter, composition, etc. may be used in a mixture, or may be coated singly in

5   order. Incidentally, in any of these methods of forming a precoating layer, when the carrier used is porous, part of the solution or dispersion or the slurry may infiltrate into the carrier via the open pores, etc.; however, it causes no problem.

10   In the above, the method of disposing alumina in carrier and the method of forming alumina-containing precoating layer on cell wall surface of carrier have been described separately. The matters common to the two methods are described below.

15   Alternate coating of an alumina powder and an alumina sol is also a preferred coating method. In this case, coating of an alumina powder and then coating of an alumina sol can allow the formed coating layer to have a dense surface; meanwhile, coating of an alumina sol and then

20   coating of an alumina powder can give higher adhesivity between carrier and coating layer. In any of these orders, an alumina sol may be used together as an inorganic binder, in coating of an alumina powder. When a plurality of alumina sources different in form, particle diameter, phase,

25   concentration, etc. are used and they are coated in order, it is preferred to coat in the order of particle size (larger particles are coated earlier) for the property of outermost layer.

    When an alumina sol is used, the content of Al_2O_3 in

30   sol is preferably 3 to 30% by mass. The reason is that a

content of less than 3% by mass invites more coating times
and a content of more than 30% by mass gives a higher
viscosity and may cause inconveniences such as easy plugging
during coating. Furthermore, 5 to 25% by mass is more

5   preferred.

When an alumina sol is used, the pH stabilizer therefor
is preferably an acid such as HCl, HNO_3, CH_3COOH or the like.
As the acid, an inorganic acid is preferred to an organic
acid and, in particular, HNO_3 is very preferable. The size

10   of the particles (colloid) constituting the alumina sol, when
the carrier is porous (for example, a ceramic-made honeycomb
structure), is selected so as to satisfy (average pore
diameter of carrier $\geqq$ average particle diameter of colloid),
preferably (average pore diameter of carrier x 10% $\geqq$ average

15   particle diameter of colloid) so that the alumina sol can
penetrate into the pores of the carrier. Specifically, the
average particle diameter of colloid is preferred to be 500
nm or less. An average diameter of 200 nm or less is more
preferred because alumina can cover the carrier surface in a

20   dense state, after firing, and an average diameter of 100 nm
or less is more preferred.

When an alumina powder is used, the particle diameters
thereof, when the carrier is porous, is preferably determined
so as to satisfy (average pore diameter of carrier $\geqq$ average

25   particle diameter of alumina powder), preferably (average
pore diameter of carrier x 30% $\geqq$ average particle diameter
of alumina powder) so that the alumina powder can penetrate
into the pores of the carrier. Specifically, the average
particle diameter of alumina powder is preferred to be 1 μm

30   or less. An average particle diameter of 0.5 μm or less is

more preferred.

When an alumina powder and an alumina sol are used as a mixture, the preferred mixing ratio thereof is (alumina powder : Al_2O_3 in alumina sol = 1:0.2 to 1:4). When the

5 alumina powder is mixed into the alumina sol so as to give a ratio of (alumina powder : Al_2O_3 in alumina sol = 1:4 or more), the effect derived from the alumina powder added can be obtained preferably; meanwhile, when the alumina sol is mixed so as to give a ratio of (alumina powder : Al_2O_3 in

10 alumina sol = 1:0.2 or more), the denseness derived from the alumina sol can be obtained preferably. The mixing ratio of the alumina powder and the alumina sol is more preferably 1:0.5 to 1:2. In this range, the meritorious effects derived from the individual substances can be obtained in a good

15 balance.

It is also preferred for coating the carrier to use the liquid obtained by mixing a powder of other material superior in corrosion resistance (e.g. mullite, zirconia, titania or SiC) instead of the alumina powder into the alumina source

20 (such as alumina sol)-containing liquid.

When coating is conducted a plurality of times using one kind of coating material or a plurality of coating materials different in form, phase, particle diameter, composition and concentration, it is possible to conduct

25 drying and firing after each coating, and it is also possible to conduct firing only once after last coating if a risk that the coating liquid applied earlier dissolves into the coating liquid applied later is small. In the latter case, it is preferred to conduct at least drying when the earlier coating

30 has been completed. When the firing is conducted only once

after last coating,the process can be simplified; while, when drying and firing are conducted in this order after each coating, different firing conditions can be set so as to match the individual coating liquids used. It is also

5 possible that precoating is completed only by drying if a risk that the coating liquid applied earlier dissolves into the coating liquid applied later is small. In this case, because the firing after coating of catalytic material is combined with the firing after coating of alumina, the

10 process can be simplified. As to the drying, rapid drying by box type drier or hot air type dryer is simple and efficient, and used suitably. When cracks on the surface of the coating become a problem, they can be alleviated by natural drying, moisture-controlled drying, vacuum freeze-drying or the like.

15 As mentioned above, after the coating, firing may be conducted after drying or without drying. As a matter of course, firing may be conducted after coating of a plurality of times, of one kind of coating material or different kinds of coating materials, or after each coating of such a coating

20 material(s). When coating is conducted a plurality of times, coating materials different in composition, form, phase, particle diameter, etc. may be used alternately. When coating is conducted a plurality of times, it is possible to conduct firing after each coating, that is, repeat coating

25 and firing. In this case, before and after the first firing, the same coating material may be used; or, before and after the first firing, coating materials different in composition, form, phase, particle diameter, etc. may be used. When firing is conducted twice, the first and second firings may

30 be conducted under the same conditions or under different

conditions.

It is also preferred to use a plurality of alumina sources different in form, phase, particle diameter, composition, concentration, etc. or an alumina source, as

5   necessary, further together with a substance liable to react with an alkali metal and a later-described alkali metal and/or alkaline earth metal, and to employ in combination with "in-carrier disposition" and "intermediate layer formation".

10   When the carrier is porous, it is preferred to reduce, by coating, the water absorption of the carrier to 20% or less, further to 10% or less. The reason is that when alumina is coated and then a catalytic material slurry containing an alkali metal is carrier thereon, the

15   infiltration of the slurry into the carrier can be suppressed by the reduced water absorption.

The method for disposing alumina in the carrier and/or on the cell wall surface of the carrier is not restricted to the above methods. In any method, when alumina has been

20   coated, there is once conducted, for example, firing at a temperature of 250℃ or more for fixation of the alumina. In order to carry a catalytic material on the alumina, it is preferred to form on the alumina a layer of a catalytic material capable of exhibiting a desired effect, for example,

25   a NO_x adsorption catalyst containing an alkali metal and/or an alkaline earth metal. Firing at 500℃ or above can promise more reliable fixation. When an alumina source other than alumina per se is used in coating alumina on the carrier, it is preferred to conduct firing at a temperature equal to

30   or higher than a temperature at which the alumina source used

is dehydrated, decomposed or oxidized to form alumina. Particularly when a coating material containing an alumina sol is coated, fixation of alumina may be conducted only by drying at 80 to 250°C because the alumina sol solidifies at

5   80 to 150°C. In this case, the process is simplified and, moreover, formation of thermal cracks on the surface of the coating can be suppressed.

Also, by controlling the firing temperature, it is possible to allow a desired alumina phase to appear. For

10   example, when an α phase of high corrosion resistance is needed, it may be obtained by coating an α-alumina powder as a raw material; however, it is also preferred to conduct firing at a temperature of 1,000°C or above in the atmosphere to form an α-alumina phase after coating using an alumina

15   powder of other phase (e.g. γ-alumina) or other alumina source, for example, alumina sol , because this can produce a dense α-alumina phase. A temperature of 1,100°C or above is more preferred because formation of α-alumina phase is accelerated. It is also preferred that the alumina phase is

20   completely an α phase, after firing. When a γ-alumina phase is desired, it is preferred to conduct firing at 900°C or below. In producing a catalyst body continuously, control of alumina phase by firing temperature is also possible in the firing step after coating of catalytic material; however, it

25   is necessary that the firing temperature is set in a range in which no deterioration of catalytic material takes place.

As described above, coating of alumina on the carrier may be conducted a plurality of times as necessary. In that case, it is possible that only impregnation or coating is

30   conducted a plurality of times with a drying step interposed

between them and firing is conducted at last, or firing is conducted even between a plurality of impregnations or coatings. In this case, the kind, properties, etc. of coating material (e.g. alumina source), the method of coating,

5 the conditions of drying and firing, etc. may each be the same or different in the plurality of times. In a preferred case, for example, in the first coating, an alumina source is impregnated or coated and then firing is conducted at a temperature of at least 1,000℃, preferably at least 1,100℃

10 to form a dense α-alumina phase, and in the second coating, an alumina source is impregnated or coated and then firing is conducted at a temperature of 900℃ or below to form a γ-alumina phase for good affinity with a catalytic material further coated thereon. When an amorphous alumina is mixed

15 into each of the γ-alumina phase and the α-alumina phase, the resulting coating can have dense surface in addition to the properties of individual alumina phases.

As to the shape of the carrier used in the present invention, there is no particular restriction. With any

20 carrier having one shape of monolithic honeycomb, pellet, bead, ring, foam, etc., the above-mentioned effect of suppression of carrier deterioration can be obtained. When there is used, of these, a honeycomb-shaped carrier (a honeycomb carrier) having a large number of throughholes

25 (cells) divided by thin partition walls, the largest effect is obtained.

Incidentally, when the present carrier is used for carrying an alkali metal thereon as a catalyst, it is also preferred to use alumina in combination with a component

30 liable to react with alkali metals (this combination use is

disclosed in JP-A-2000-279810) because the combination use gives an even higher effect of suppression of carrier deterioration. For example, when alumina is combined with silica liable to react with alkali metals and coating on the
5   carrier is made first with silica and then with alumina thereon, alumina (an anti-corrosive material) can protect the carrier against the K diffusing from a catalyst layer and lastly silica can trap K diffusing into a carrier; thus, the protection of the carrier can be made in two-stage different
10   actions.

It is also preferred to use alumina in combination with at least one kind of alkali metal and/or alkaline earth metal according to the method described in JP-A-2002-282702 (invented by the present inventors), because this combination
15   use gives an even higher effect of suppression of carrier deterioration. When alumina is used with potassium silicate (K_2SiO_3) (containing an alkali metal) or barium oxide (containing an alkaline earth metal), the protection of the carrier can be made in different two-stage actions, for
20   example, by coating of potassium silicate on alumina or coating of alumina on barium oxide. Alternatively, it is possible to use alumina together with the at least one kind of alkali metal and/or alkaline earth metal. Therefore, the description of JP-A-2002-282702 is incorporated herein by
25   reference.

Also when alumina is used in combination with the above-mentioned substance liable to react with an alkali metal and/or an alkaline earth metal both used as a catalyst component, and/or with the above-mentioned alkali metal
30   and/or alkaline earth metal, a more preferred result is

obtained by using substantially a sol alone for all the coating materials (e.g. silica) other than alumina.

When a plurality of components different in function are coated as mentioned above, the individual functions are exhibited more effectively by coating them separately, for example, in layers; however, when a plurality of components same in function are coated, they may be coated in mixture, of course.

The present invention exhibits its effect when applied to various carrier materials; therefore, there is no particular restriction as to the material of carrier and it may be a ceramic, a metal, etc. The present invention can be preferably applied to, for example, an oxide type ceramic material such as cordierite, mullite, alumina, zirconia, titania, spinel, zirconyl phosphate, aluminum titanate, Ge-cordierite or the like; a non-oxide type ceramic material such as SiC, SiN or the like; and a metal material such as Fe-Cr-Al alloy or the like. When there is used, in particular, an oxide type ceramic carrier liable to be corroded by alkali metals and alkaline earth metals, a large effect is obtained, and the present invention is very effective to a cordierite carrier widely used in catalysts for purification of automobile exhaust gas. The present invention is also applicable preferably to carriers of mixture or composite type, made of two or more kinds of materials; for example, carriers made of a material obtained by bonding mullite particles or SiC particles with cordierite, particularly a carrier containing 10% or more of cordierite as a component.

The shape of through-holes (cells) of honeycomb carrier

may be any of a circle, a polygon, a corrugation, etc. The external shape of honeycomb carrier can be made so as to have a desired shape fitting with the internal shape of an exhaust gas system in which the carrier is provided.

5   As to the cell density of honeycomb carrier, there is no particular restriction, either. However, the cell density is preferably 6 to 1,500 cells/in.^{2} (0.9 to 233 cells/cm^2) when the carrier is used as a catalyst carrier. The thickness of the partition wall of honeycomb carrier is

10   preferably 20 to 2,000 μm. The diffusion of alkali metal and/or alkaline earth metal from catalytic material to partition wall center of carrier is easy in the case that the partition wall is a thin wall of 20 to 200 μm in the thickness. Therefore, the necessity of the present invention

15   becomes high, and the effect of suppression of carrier deterioration also becomes large.

There is no particular restriction, either, as to the porosity of honeycomb carrier. However, when the porosity is 10% or more, further 20% or more, the diffusion of alkali

20   metal and/or alkaline earth metal through open pores of carrier is easy; therefore, the necessity of the present invention is high; and the effect of suppression of carrier deterioration is large. Incidentally, the thermal expansion coefficient of the carrier after coating is preferably

25   8.0x10^{-6} /℃ or less, more preferably 4.0x10^{-6} /℃ or less, in view of the thermal shock resistance required for the catalyst body for automobile exhaust gas. A thermal expansion coefficient of 2.0x10^{-6} /℃ or less enables mounting of catalyst body at a position near engine.

30   The amount of alumina disposed on the carrier is

preferably 0.5 to 200 g /liter (unit volume of catalyst body).
When the amount is less than 0.5 g/liter, the resulting
effect of suppression of carrier deterioration is small; when
a amount of more than 200 g/liter is coated on the same

5   carrier as NO_x adsorption catalyst, the clogging of cells may
occur when the carrier is a honeycomb carrier. The amount is
more preferably 10 to 100 g/liter, further preferably 30 to
80 g/liter. 40 to 70 g/liter is particularly preferred from
the standpoint of the balance between prevention of crack

10   generation and suppression of flexural strength decrease and
pressure loss. Needless to say, the above amount of alumina
does not contain the amount of the alumina used as a matrix
material of high specific surface area for highly dispersing
a catalytic active component (represented by a noble metal or

15   the like) which is used depending upon the application of
obtained catalyst body.

     The thickness of alumina layer formed on the carrier
shall be 20 μm or less after firing, preferably 10 μm or less,
when measured at a section vertical to the axial direction of

20   carrier with one side of a partition wall of carrier cell
around the center of the partition wall using an electron
microscope. A thickness of more than 20 μm is not preferred
because of an increased pressure loss.

     The viscosity of any coating liquid represented by

25   alumina sol is ordinarily 10,000 mPa.s or lower, preferably
500 mPa.s or less, further preferably 30 mPa.s or lower. A
viscosity higher than 10,000 mPa.s may make coating difficult
when the carrier is a honeycomb body. A viscosity higher
than 500 mPa.s may cause the clogging of cells depending upon

30   the carrier used, which needs care. A viscosity of 30 mPa.s

or lower is preferred because the coating liquid infiltrates appropriately even into the pores of carrier and a dense alumina layer of high adhesivity is formed.

The pH of alumina sol is ordinarily 2.0 to 6.0, preferably 3.0 to 5.0. A pH lower than 2.0 is not preferred because the carrier is corroded by immersion in the coating liquid when the carrier is not an acid-resistant material. With a pH higher than 6.0, the particles in sol may cause agglomeration.

Alumina may contain other metal and/or a metal oxide, a carbide, a nitride, etc. as long as they do not impair the action of alumina intended by the present invention. However, it is preferred that alumina contains no noble metal as catalyst, or the like in view of the high-temperature stability. Further, in order to effectively protect the carrier from, for example, alkali metals and/or alkaline earth metals, it is more preferred that alumina is formed as a single alumina layer between the carrier and a catalyst layer containing at least an alkali metal and/or an alkaline earth metal. In other words, between the carrier and a catalyst layer containing an alkali metal and/or an alkaline earth metal, substantially an alumina layer alone may be formed, or, as described later, alumina may be laminated on and/or beneath a composite or mixed layer of alumina and other component. As a matter of course, in producing a catalyst body, the catalyst layer formed may contain a catalyst other than so-called NO_x catalyst, for example, a noble metal (e.g. Pt, Pd and/or Rh) for combustion of hydrocarbon, etc. Further, a separate catalyst layer containing a noble metal (e.g. Pt, Pd and/or Rh) may be

formed on a NO_x catalyst layer, with no restriction.

The catalyst body of the present invention may be applied together with other purification materials applied to exhaust gas systems, such as NO_x adsorption catalytic

5   material comprising other components, different kind of catalytic material represented by three-way catalyst, co-catalyst represented by Ce oxide and/or Zr oxide, HC adsorption material, and the like. In that case, these other purification materials may be mixed into the catalytic

10   material of the present catalyst body, but they are preferred to be laminated thereon in layers for higher heat resistance. Alternatively, they may be separately disposed on the upstream/downstream portions of the present catalyst body. Further alternatively, one may arbitrarily use the present

15   catalyst body by combining it with those materials prepared as independent bodies in an exhaust gas system.

[Examples]

The present invention is described more specifically below by way of Examples. However, the present invention is

20   in no way restricted by these Examples.

[Preparation of slurries for alumina coating]

Slurry A for alumina coating:

A commercial Al_2O_3 sol and water were added to a commercial γ-Al_2O_3 powder (specific surface area: 200 m^2/g).

25   The mixture was pulverized in a pot mill to prepare slurry A for alumina coating. The amount of the Al_2O_3 sol added was such that the solid content (the weight of Al_2O_3 contained in the Al_2O_3 sol) thereof took 50% by mass of the total Al_2O_3 in slurry, and water was appropriately added so that the slurry

30   could have a viscosity allowing easy coating.

Slurries Bs for alumina coating:

Slurries B1, B2 and B3 for alumina coating were obtained in the same manner as in preparation of slurry A for alumina coating except that an α-Al_2O_3 powder was used in
5   place of the commercial γ-Al_2O_3 powder and the ratio of the Al_2O_3 amounts in the α-Al_2O_3 powder and the Al_2O_3 sol was set at three levels of 1:1, 1:0.1 and 1:0.3.

Slurry B4 for alumina coating:

Slurry B4 for alumina coating was obtained in the same
10   manner as in preparation of slurry A for alumina coating except that, to a commercial α-Al_2O_3 powder, 10% by mass in term of the superaddition of an organic binder of acrylic type (ARON AS-7503, a product of Toagosei Co., Ltd.) and an appropriate amount of water were added.

15   Slurry C for alumina coating:

Slurry C for alumina coating was obtained in the same manner as in preparation of slurry A for alumina coating except that a 1:1 mixture of an α-Al_2O_3 powder and a mullite powder was used in place of the commercial γ-Al_2O_3 powder and
20   the ratio of the Al_2O_3 amounts in the 1:1 mixture of an α-Al_2O_3 powder and a mullite powder and the Al_2O_3 sol was set at 1:1.

[Preparation of slurry for coating of NO_x adsorption catalyst]

25   A commercial γ-Al_2O_3 powder (specific surface area: 200 m^2/g) was immersed in a mixed solution of a $(NH_3)_2Pt(NO_2)_2$ aqueous solution and a KNO_3 aqueous solution. The mixture was stirred in a pot mill for 2 hours; then, water was removed by vaporization to dryness; the residue was dry-
30   disintegrated and fired in an electric oven at 600°C for 3

hours. To the resulting (Pt + K)-predoped γ-Al_2O_3 powder were added a commercial Al_2O_3 sol and water, and the mixture was wet-ground in a pot mill to prepare a slurry for coating. The ratio of γ-Al_2O_3, Pt and K amounts was adjusted at the

5   stages of preparation of the mixed solution and immersion of γ-Al_2O_3 powder therein so that when the slurry was coated on a honeycomb carrier, final firing was completed, and the amount of NO_x adsorption catalyst coated was 100 g per liter of honeycomb volume, the weight of Pt element became 30 g per

10   ft^3 of honeycomb volume (1.06 g per liter) and the weight of K element became 20 g per liter of honeycomb volume. The Al_2O_3 sol was added in such an amount that its solid content (Al_2O_3 amount) became 5% by mass of the total Al_2O_3 amount in the obtained slurry, and water was added appropriately so

15   that the slurry could have a viscosity allowing easy coating.
[Preparation of samples]
(Example 1)

First, a cordierite honeycomb carrier [partition wall thickness: 6 mil (0.15 mm), cell density: 400 cpsi (62

20   cells/cm^2), porosity: 30%] was immersed in a commercial Al_2O_3 sol. The excessive liquid in the carrier cells was removed by blowing and the resulting carrier was dried. The amount of the Al_2O_3 sol coated was adjusted so as to become 70 g per liter of honeycomb carrier volume, after firing. When the

25   amount coated was short after one time immersion and drying, immersion and drying was repeated until the intended amount was reached. The resulting honeycomb material, which was a so-called primary carrier having alumina coated thereon (hereinafter referred to simply as alumina-coated carrier),

30   was fired in an electric oven at 600°C for 1 hour. After the

firing, the honeycomb material was coated with the above-
mentioned slurry for coating of NO_x adsorption catalyst
(hereinafter, abbreviated as "NO_x adsorption catalyst
slurry"), followed by drying. This step (coating and drying)
5   was as necessary repeated until the amount of the NO_x
adsorption catalyst coated became 100 g per liter.
Thereafter, firing was again conducted in an electric oven at
600℃ for 1 hour to obtain NO_x adsorption catalyst body 1.
(Example 2)

10   NO_x adsorption catalyst bodies 2(a), 2(b) and 2(c) were
obtained in the same manner as in Example 1 except that the
firing conditions after coating of Al_2O_3 sol were 1,200℃ and
3 hours and that the amount of the Al_2O_3 sol coated was
adjusted so as to become, respectively, 70 g per liter of
15   honeycomb carrier volume, 30 g per liter, and 90 g per liter,
after firing to produce NO_x adsorption catalyst bodies 2(a)
to 2(c).
(Example 3)

        NO_x adsorption catalyst body 3 was obtained in the same
20   manner as in Example 1 except that slurry A for alumina
coating (which was a 1:1 mixture of a γ-alumina powder and
an alumina sol) was used in place of the commercial Al_2O_3 sol.
The use amount of slurry A for alumina coating was adjusted
so that the total of the Al_2O_3 derived from the γ-Al_2O_3 powder
25   and the Al_2O_3 derived from the Al_2O_3 sol became 70 g per liter
after firing.
(Example 4)

        NO_x adsorption catalyst body 4 was obtained in the same
manner as in Example 3 except that the firing conditions
30   after coating of slurry A for alumina coating were 1,200℃

and 3 hours.

(Example 5)

NO$_x$ adsorption catalyst bodies 5(a), 5(b), 5(c), 5(d) and 5(e) were obtained in the same manner as in Example 3 except that NO$_x$ adsorption catalyst body 5(a) was produced by using slurry B1 for alumina coating in place of slurry A for alumina coating and conducting firing at 600℃ for 1 hour and that NO$_x$ adsorption catalyst bodies 5(b) to 5(e) were produced by using slurries B1, B2, B3 and B4 for alumina coating, respectively, and conducting firing at 1,200℃ for 3 hours.

(Comparative Example and Reference Example)

The same cordierite honeycomb material as used in Example 1 was coated with the NO$_x$ adsorption catalyst slurry, followed by drying. This step (coating and drying) was as necessary repeated until the amount of the NO$_x$ adsorption catalyst coated became 100 g per liter. Thereafter, firing was conducted in an electric oven at 600℃ for 1 hour to obtain NO$_x$ adsorption catalyst body 6.

(Example 6)

NO$_x$ adsorption catalyst body 7 was obtained in the same manner as in Example 1 except that there were repeated two times the immersion of cordierite honeycomb carrier in Al$_2$O$_3$ sol, the drying of carrier, and the firing of honeycomb material in electric oven at 600℃ for 1 hour. The amount of the Al$_2$O$_3$ sol coated was adjusted so as to become 70 g per liter in total after two times of firing.

(Example 7)

NO$_x$ adsorption catalyst bodies 8(a) to 8(m) were obtained in the same manner as in Example 2 except that the

immersion of cordierite honeycomb carrier, the drying of carrier, the conditions of firing of honeycomb material in electric oven, and the amount of coating were as shown in Table 1 and Table 2.

Table 1

Catalyst body No.	8(a)	8(b)	8(c)	8(d)	8(e)	8(f)	8(g)
Kind of coating material	Alumina sol	Alumina sol	Alumina sol	α-alumina powder + alumina sol	α-alumina powder + alumina sol	α-alumina powder + mullite powder +alumina sol	Alumina sol
Mixing ratio	-	-	-	1:1	1:1	0.5:0.5:1	-
First firing conditions	1200°C, 3 hours	600°C, 1 hour	1200°C, 1 hour	1200°C, 3 hours	-	1200°C, 3 hours	1200°C, 3 hours
Kind of coating material	Alumina sol	Alumina sol	Alumina sol	Alumina sol	Alumina sol	Alumina sol	γ-alumina powder + alumina sol
Mixing ratio	-	-	-	-	-	-	1:1
Second firing conditions	1200°C, 3 hours	1200°C, 3 hours	600°C, 1 hour	600°C, 1 hour	600°C, 1 hour	600°C, 1 hour	600°C, 1 hour
Total amount of alumina coated	70 g/liter	70 g/liter	70 g/liter	70 g/liter	70 g/liter	50 g/liter (mullite: 20 g/liter)	70 g/liter

Table 2

Catalyst body No.	8(h)	8(i)	8(j)	8(k)	8(l)	8(m)
Kind of coating material	Silica sol	Alumina sol	Silica sol	Silica sol	Silica sol + alumina sol	Silica sol + alumina sol
Mixing ratio	-	-	-	-	2:5	2:5
First firing conditions	600℃, 1 hour	1200℃, 3 hours	-	-	1200℃, 3 hours	1200℃, 3 hours
Kind of coating material	Alumina sol	Silica sol	Alumina sol	Alumina sol	-	Alumina sol
Mixing ratio	-	-	-	-	-	-
Second firing conditions	600℃, 1 hour	600℃, 1 hour	600℃, 1 hour	1200℃, 3 hours	-	1200℃, 3 hours
Total amount of alumina coated	30 g/liter (silica: 40 g/liter)	30 g/liter (silica: 40 g/liter)	30 g/liter (silica: 40 g/liter)	30 g/liter (silica: 40 g/liter)	50 g/liter (silica: 20 g/liter)	60 g/liter (silica: 10 g/liter)

[Durability test]

The above-obtained NO_x adsorption catalyst bodies 1, 2, 3(a) to 3(c), 4, 5(a) to 5(e), 6, 7, and 8(a) to 8(m) were subjected to an accelerated durability test at 850℃ for 30
5   hours in an electric oven with 10% of moisture.

Also, for reference, a cordierite honeycomb carrier having nothing coated thereon was subjected to the same accelerated durability test.

[Evaluation for effect of suppression of carrier
10 deterioration]

NO_x adsorption catalyst bodies 1, 2, 3(a) to 3(c), 4, 5(a) to 5(e), 6, 7, and 8(a) to 8(m) and NO_x adsorption catalyst body 6 (Comparative Example) were examined for the degree of cracking after durability test, by appearance
15 observation and fine structure observation by electron microscope. Incidentally, as to the degree ofcracking, no crack was reported as 0 and generation of crack which was regarded to become a problem in practical application, was reported as 10; thus, the degree of cracking was evaluated in
20 11 levels. Further, initial flexural strength and after-durability-test flexural strength were compared. The results thereof are shown in Table 3.

25

30

Table 3

Example, Comparative Example, etc.	No. of NO_x adsorption catalyst body	Degree of crack generation (after durability test)	Reduction in flexural strength (%) *
Example 1	1	4	34
Example 2	2(a)	3	25
Example 2	2(b)	6	46
Example 2	2(c)	3	23
Example 3	3	5	40
Example 4	4	4	32
Example 5	5(a)	4	36
Example 5	5(b)	3	31
Example 5	5(c)	6	51
Example 5	5(d)	5	38
Example 5	5(e)	8	66
Example 6	7	3	27
Example 7	8(a)	2	18
Example 7	8(b)	2	22
Example 7	8(c)	1	19
Example 7	8(d)	1	25
Example 7	8(e)	3	30
Example 7	8(f)	1	25
Example 7	8(g)	1	28
Example 7	8(h)	1	7
Example 7	8(i)	1	14
Example 7	8(j)	1	7
Example 7	8(k)	0	3
Example 7	8(l)	1	9
Example 7	8(m)	0	5
Comparative Example	6	10	74
Reference Example	-	0	1

* : Reduction in flexural strength (%) = [(initial strength - after-durability-test strength)/initial strength] x 100

It is appreciated from Table 3 that each of NO_x adsorption catalyst bodies 1, 2, 3(a) to 3(c), 4, 5(a) to 5(e), 7, and 8(a) to 8(m) (Examples 1 to 7) according to the present invention, as compared with NO_x adsorption catalyst

5   body 6 free from alumina (Comparative Example), is low in cracking of carrier and also in reduction in strength. The results of Table 3 indicate that when alumina alone is disposed, use of an alumina sol, as compared with mixed use of an alumina powder and an alumina sol, tends to give a

10   superior NO_x adsorption catalyst body. Among different alumina powders, use of organic binder gives no satisfactory effect as compared with no use of organic binder; and an α-alumina powder tends to give a superior effect as compared with a γ-alumina powder. As to firing conditions, firing at

15   1,200℃ (a higher temperature) is preferred and two-times firing gives a superior result as compared with one-time firing. Further, it is clear that combined disposition of silica and alumina gives a superior NO_x adsorption catalyst body.

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Industrial Applicability

As described above, in the catalyst body of the present invention, there are disposed, in the carrier and/or on the cell wall surface of the carrier, an alumina low in

25   reactivity with an alkali metal and/or an alkaline earth metal both used as a catalyst component, and, optionally, a substance liable to react with an alkali metal and/or an alkaline earth metal both used as a catalyst component and/or an alkali metal and/or an alkaline earth metal; thereby, the

30   carrier, even when exposed to high temperatures, is protected

by the alumina from the alkali metal and/or the alkaline
earth metal both present in the catalytic material of the
catalyst body, and the reaction between these metals with the
carrier is suppressed. As a result, the deterioration of
carrier caused by alkali metal and/or alkaline earth metal is
suppressed, and the present catalyst body, even when used
over a long period of time with the carrier coating thereon a
catalytic material such as mentioned above, can withstand
such use.